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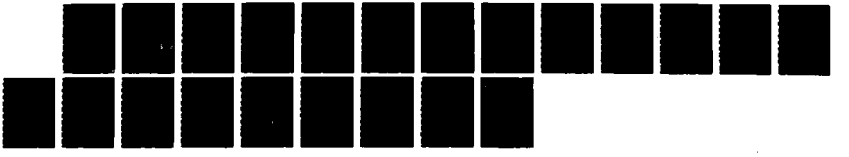

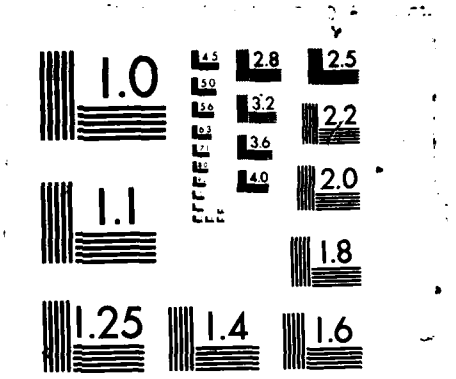

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A High Pressure Inductively Coupled Plasma Torch

by

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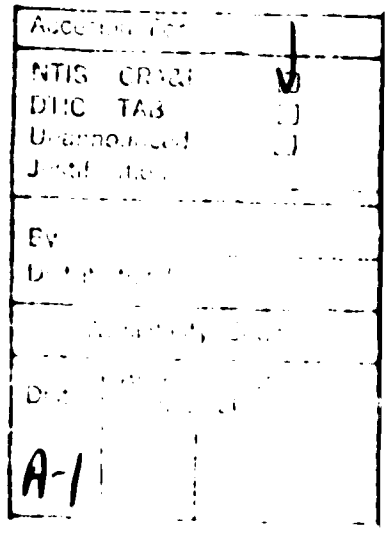

A HIGH PRESSURE INDUCTIVELY COUPLED PLASMA TORCH

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Index Headings: Emission spectroscopy, ICP; Instrumentation, torch design

ABSTRACT

An Inductively Coupled Plasma (ICP) torch utilizing an extended coolant tube that tapers down to a small exit orifice designed to increase the pressure within the ICP torch is described. This torch design makes use of the advantages associated with higher torch operating pressures, including improved detection limits, increased sensitivity and better plasma stability, without requiring major modifications to existing commercially available ICP torch box and matching networks. Detection limits obtained utilizing the new torch design are compared to those obtained from several commonly used torch designs using a commercially available torch box and spectrometer. A two- to seven-fold improvement in detection limits is observed through increasing torch operating pressure from 101.325 KPa (760 torr, or atmospheric pressure) to 120 KPa (900 torr).

INTRODUCTION

Since its introduction by REED in 1961 [1,2] and subsequent modification by Greenfield et al. [3,4] and Fassel et al. [5], the inductively coupled plasma torch has remained substantially unchanged. The typical inductively coupled plasma torch consists of three concentric tubes. The center tube delivers a sample gas flow containing the analyte as an aerosol. The second tube, for the auxiliary (or plasma) gas flow, is used to supplement the main gas flow and help stabilize the plasma. The outer tube carries the plasma support gas flow (or coolant gas).

Over the years, many variations on the basic torch design have been proposed [6-16]. All of the designs have one common feature, they are all open to the atmosphere and therefore the plasma is formed in a region that is essentially at atmospheric pressure. The two exceptions to this are a reduced pressure torch design proposed by SELISKAR and WARNER [17] and a variable pressure torch used by SMITH and DENTON [18].

Increasing the pressure within the torch has an effect on the intensity of the emissions from an analyte species. Higher excitation temperatures can be obtained through the use of increased torch pressures. These higher excitation temperatures lead to higher analyte emission intensities. Studies using the variable pressure torch system have shown that an increase in the Mg(II) 279.533 nm emission intensity can be obtained by increasing the torch pressure from 101.325 KPa (760 torr, or atmospheric pressure) to 200 KPa (1500 torr)(see Figure 1). In addition, no associated increase in background intensity at the wavelength of interest was observed, indicating an increase in sensitivity and a possible improvement in detection limits. A new style of ICP torch has been designed that fits in a

standard ICP torch box and allows the use of high torch pressure with commercially available spectrometers.

INSTRUMENTATION

Three different torch designs were used in this study. The first was a standard torch design where the end of the coolant tube is cut off at the top of the load coil. The plasma is formed above the end of the coolant tube and therefore the pressure where the plasma is formed is controlled by the pressure in the room. A quartz bonnet was used with this torch to reduce arcing to the load coil. The second torch design utilizes an "extended" coolant tube. The quartz coolant tube extends past the load coil so that the plasma is formed within the coolant tube. The end of the coolant tube is open to the room so the pressure within the torch is still dictated by atmospheric pressure. This torch design has been shown by WINDSOR [19] to increase the stability of the plasma and reduce entrainment of air. This torch design was included in the study to better determine whether the change in detection limits observed was due to the increased torch pressure or simply due to the increased stability obtained by enclosing the plasma within the coolant tube. The new torch design is similar to the "extended" coolant tube torch, except that the end of the tube has been tapered down to an orifice which restricts the gas flow from the torch and builds up a back pressure within the torch (see Figure 2). The torch pressure can be controlled over a limited range by adjusting the gas flows entering the torch. The range of pressures obtainable with the torch can be altered by changing the size of the exit orifice. The torch used in this study had a two millimeter exit orifice and operated at an internal torch pressure of 120 KPa (900 torr). It should be noted that the length of the

high pressure torch coolant tube is not critical as long as the orifice is far enough above the plasma so that it does not melt while the plasma is operating.

The pressure within the torch was monitored with a Helicoid Gage Co. pressure gage that covered the range 0-1500 torr absolute pressure with a certified accuracy of ±0.25%, the pressure gage was connected in the auxiliary gas line running to the torch. A 13 KPa (100 torr) increase in torch pressure was observed with the ignition of the plasma due to the temperature increase of the gas. No significant drift was observed in torch pressure once a stable plasma was obtained.

The spectrometer used in these studies was a Spectrametrics SpectraSpan IIIB simultaneous multi-element analyzer (Spectrametrics, Inc., 204 Andover Street, Andover, MA) with a Plasma Therm Inc. (Rte 73, Kresson, NJ) model HFP 2500D RF generator and torch box. A demountable torch base was constructed similar to that described by WINDSOR et al. [12], to allow easy interchange of coolant tubes for comparison of torch designs.

A sample introduction system was built to achieve uniform sample delivery to the nebulizer independent of torch, or nebulizer chamber, pressure. The system consists of a large chamber made from a 30.5 cm piece of 10 cm I.D. Corning glass pipe (Corning Glass Co., Corning, NY 14830), one end of which was sealed with a brass flange. This flange was fitted with a feed through to allow the sample tube to pass through the flange. The other end of the glass pipe is sealed with a model SVS-4I gate valve (General Technology Corp., Hayward, CA 94546) to allow sample vials to be placed inside and then the chamber to be closed and pressurized. By pressurizing the sample holding chamber to 32 psi and using a Cole-Parmer (Chicago, IL) model 7553-00 peristaltic pump, a constant sample delivery to the nebulizer

over the pressure range of interest can be maintained. The construction of a pressure chamber was necessary because the peristaltic pump alone was not capable of maintaining a constant flow over the desired pressure range.

The nebulizer used was a sealed crossflow type built in house and designed to operate with the nebulizer spray chamber at the same pressure as the torch. For this reason, the waste trap and nebulizer spray chamber were constructed as a closed system (see Figure 3). Though a special high pressure sealed nebulizer and pressured sample chamber were used for this study, to insure a constant sample uptake with each torch design tested, there is no reason to believe that the high pressure torch could not be used with the standard nebulizer configuration present in most commercially available ICP spectrometers with only minor modifications necessary to adjust for the fact that the nebulizer chamber would be at greater than atmospheric pressure. The spray chamber would have to be modified to be a closed system with the waste trap, and a peristaltic pump would be needed for pumping sample to the nebulizer.

The demountable torch base was constructed from three brass Cajon Ultra-Torr fittings modified to hold a 20.5 mm O.D. quartz coolant tube, a 12 mm O.D. plasma tube and a 6 mm O.D. sample tube. All tubes were GE type 214 quartz (General Electric Co., Syracuse, NY). The torch base design allows easy changing and replacement of all tubes. Proper tube alignment was maintained by the use of Teflon spacers.

EXPERIMENTAL

The detection limits for several elements were determined using each of the three torch configurations. In all cases, gas flow and viewing position were optimized. The method used to calculate the detection limit was that

recommended by the instrument manufacturer [20]. The detection limit is defined as the analyte concentration corresponding to a signal level equal to three times the standard deviation of the background at the wavelength of interest and is determined from the average of three sets, each of nine ten-second integrations at the wavelength of interest. In addition, the background equivalent concentration (BEC) was determined, and an estimate of precision was made. BEC is the analyte concentration which is equivalent to the signal generated by the plasma and matrix, without analyte present, at the analyte emission wavelength. The BEC is determined by measuring the difference between the signal from the blank solution and the signal obtained with the spectrometer entrance slit blocked at the analytical wavelength. The BEC is the inverse of the signal-to-background ratio, expressed in concentration units. The estimate of precision is determined from the relative standard deviation of nine ten-second integrations on a sample 5 to 10 times the BEC. Table I lists standard operating conditions recommended by the manufacturer for the collection of detection limit data. Conditions used in this study differed from these only in that the sample uptake rate used with the sealed nebulizer was 1.35 mL/min and all flow rates were optimized for each torch configuration.

RESULTS AND DISCUSSION

The detection limits for Mg, Zn and Fe were measured with each torch configuration. Table II presents the ratios of the results obtained with the extended torch and the high pressure torch relative to the results obtained with the stock torch design. The presentation of the ratios allows

one to quickly determine the expected improvement in detection limits obtainable on any ICP system. By using the new torch design operating at 120 KPa (900 torr), a significant improvement in detection limits for all three metals, over those obtained at atmospheric pressure using the stock torch configuration, was observed. A two- to seven-fold decrease in detection limits was obtained (depending on the element). These results are consistent with the increase in emission intensity observed in earlier studies performed at increased torch pressures [18].

The spectrometer used in this study was equipped with an auto-ranging electrometer. The increased sensitivity manifests itself in the form of lower amplifier scales being used by the electrometer. In the absence of changes in the background due to the presence of molecular bands or other spectral interferences, this change in amplifier scale will lead to a decrease in the BEC relative to that of the extended tube torch.

The results demonstrate that this new torch design can be used to improve the detection limits obtainable with ICP-AES. The decrease in detection limits observed is due primarily to the increase in signal intensity occurring with increased pressure. This increase in emission intensity is due to an increase in excitation temperature and associated increase in population of the excited states in the analyte within the plasma. Earlier studies [18] have indicated an increase in electron density and a possible shift towards local thermal equilibrium (LTE) with increasing torch pressure. The shift towards LTE conditions within the plasma means a more efficient transfer of energy from the argon support gas to the analyte species present in the central channel of the plasma, leading to an increase in signal intensity.

An improvement in plasma stability associated with the high pressure torch was also observed because of its enclosed design. By containing the plasma within the coolant tube, plasma drift and flicker are reduced. A similar increase in stability was observed with the extended tube torch.

This new torch design could lead the way for a generation of ICP torches that are capable of better sensitivity and improved detection limits through the utilization of a previously overlooked operating parameter, pressure.

ACKNOWLEDGMENT

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REFERENCES

1. T.B. Reed, J. Appl. Phys. 32, 821 (1961).
2. T.B. Reed, J. Appl. Phys. 32, 2534 (1961).
3. S. Greenfield, U.S. Pat. 3,467,471. 1969.
4. S. Greenfield, I.L.W. Jones, and C.T. Berry, Analyst 89, 713 (1964).5. R.H. Wendt and V.A. Fassel, Anal. Chem. 37, 920 (1965).
6. K. Ohls and K. Krefta, ICP Information Newsletter 1, 168 (1976).
7. F.E. Lichte and S.R. Koirtyohann, ICP Information Newsletter 1, 200 (1976).
8. C.D. Allemand and R.M. Barnes, Appl. Spectrosc. 31, 434 (1977).
9. J.M. Mermet and C. Trassy, Appl. Spectrosc. 31, 237 (1977).
10. R. Barnes, ICP Information Newsletter 1, 49 (1975).
11. J.L. Genna, R.M. Barnes and C.D. Allemand, Anal. Chem. 49, 1450 (1977).
12. D.L. Windsor, D.R. Heine and M.B. Denton, Appl. Spectrosc. 33, 56 (1979).
13. R. Rezaaiyaan, G.M. Hieftje, H. Anderson, H. Kaiser and B. Meddings, Appl. Spectrosc. 36, 627 (1982).
14. R.N. Savage and G.M. Hieftje, Anal. Chem. 51, 408 (1979).
15. C.D. Allemand and R.M. Barnes, Anal. Chem. 51, 2392 (1979).
16. A.D. Weiss, R.N. Savage and G.M. Hieftje, Anal. Chim. Acta 124, 245 (1981).
17. C.J. Seliskar and D.K. Warner, Appl. Spectrosc. 39, 181 (1985).
18. T.R. Smith and M.B. Denton, Spectrochim. Acta 40B (9), 1227 (1985).
19. D.L. Windsor, "Use of the Inductively Coupled Plasma for the Elemental Analysis of Organic Compounds," Ph.D. Dissertation, University of Arizona (1977), p. 120.

20. "Handbook of Spectral Line Characteristics for the Inductively Coupled Plasma Echelle Spectrometer Systems," A.W. Boorn, Ed., Spectrametrics, Inc., Andover, MA.

TABLE I

SpectraSpan ICP Standard Conditions [20]

Rf Power	1.25 kW
Plasma Gas	12 L/min
Auxiliary Gas	0.4 L/min
Nebulizer Gas	24 psig
Nebulizer	Concentric glass
Sample uptake	2.5 mL/min
Entrance slit	50 X 300 μm
Exit slit	100 X 300 μm
PMT voltage	-900 volts

TABLE II

Torch Performance Results
(Results are relative to the stock torch configuration.)

Torch	Estimate of Precision[a]	BEC[b]	Detection Limit[c]
	Mg(II) 279.533 nm		
Extended Torch	0.90	1.40	0.54
High Pressure Torch (120 KPa)	0.42	0.76	0.38
	Zn(I) 213.856 nm		
Extended Torch	0.42	0.10	0.70
High Pressure Torch (120 KPa)	0.25	0.08	0.17
	Fe(I) 238.204 nm		
Extended Torch	0.47	0.27	0.86
High Pressure Torch (120 KPa)	0.15	0.13	0.14

[a] $\frac{\%RSD_{standard}}{\%RSD_{test\ torch}}$

[b] $\frac{BEC_{standard}}{BEC_{test\ torch}}$

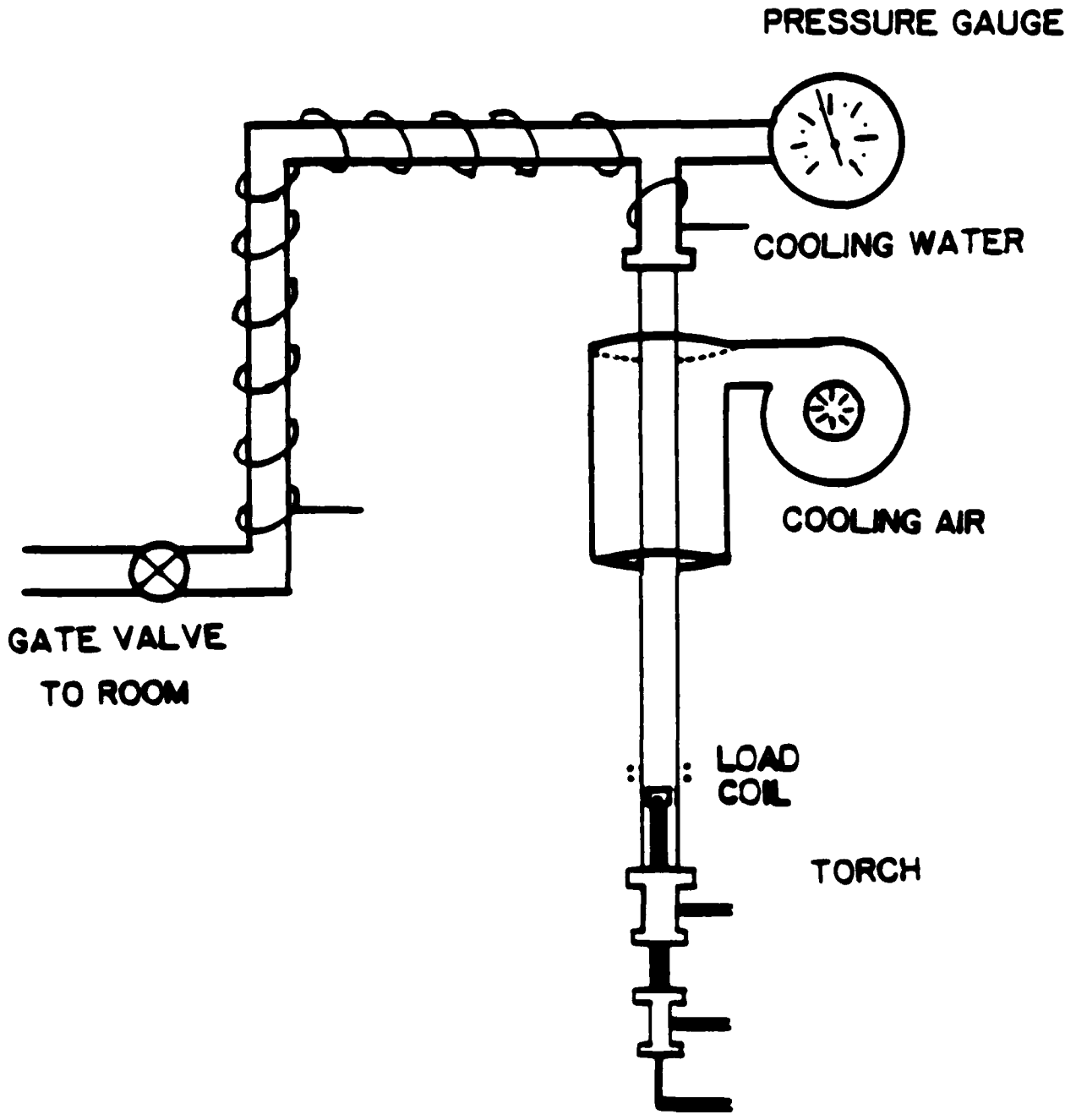
[c] $\frac{DL_{standard}}{DL_{test\ torch}}$

FIGURE CAPTIONS

Figure 1: Variable Pressure Torch

Figure 2: Fixed High Pressure Torch

Figure 3: High Pressure Nebulizer System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COOLING WATER
COOLING AIR
GATE VALVE
TO ROOM
LOAD
COIL
TORCH

Figure

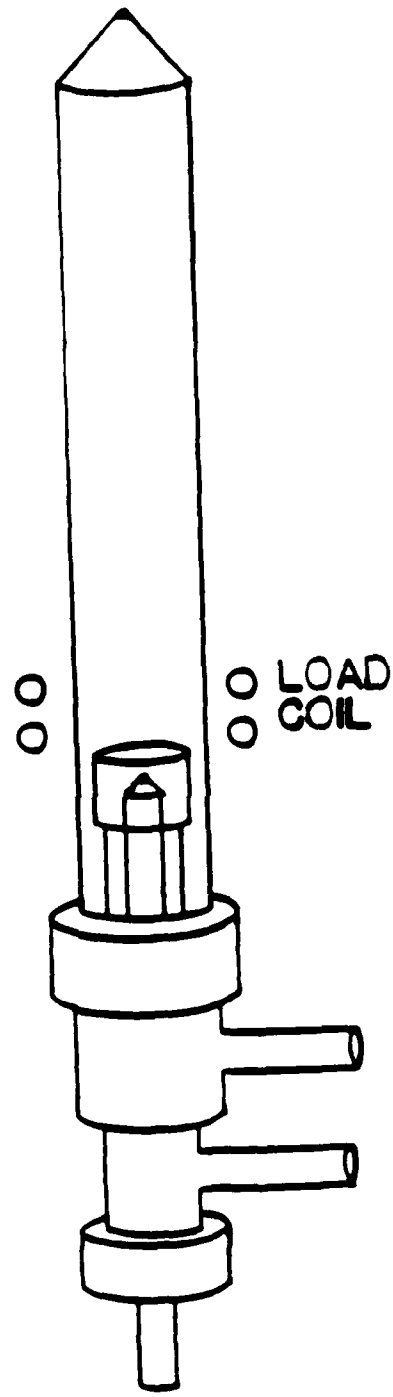

Figure 2

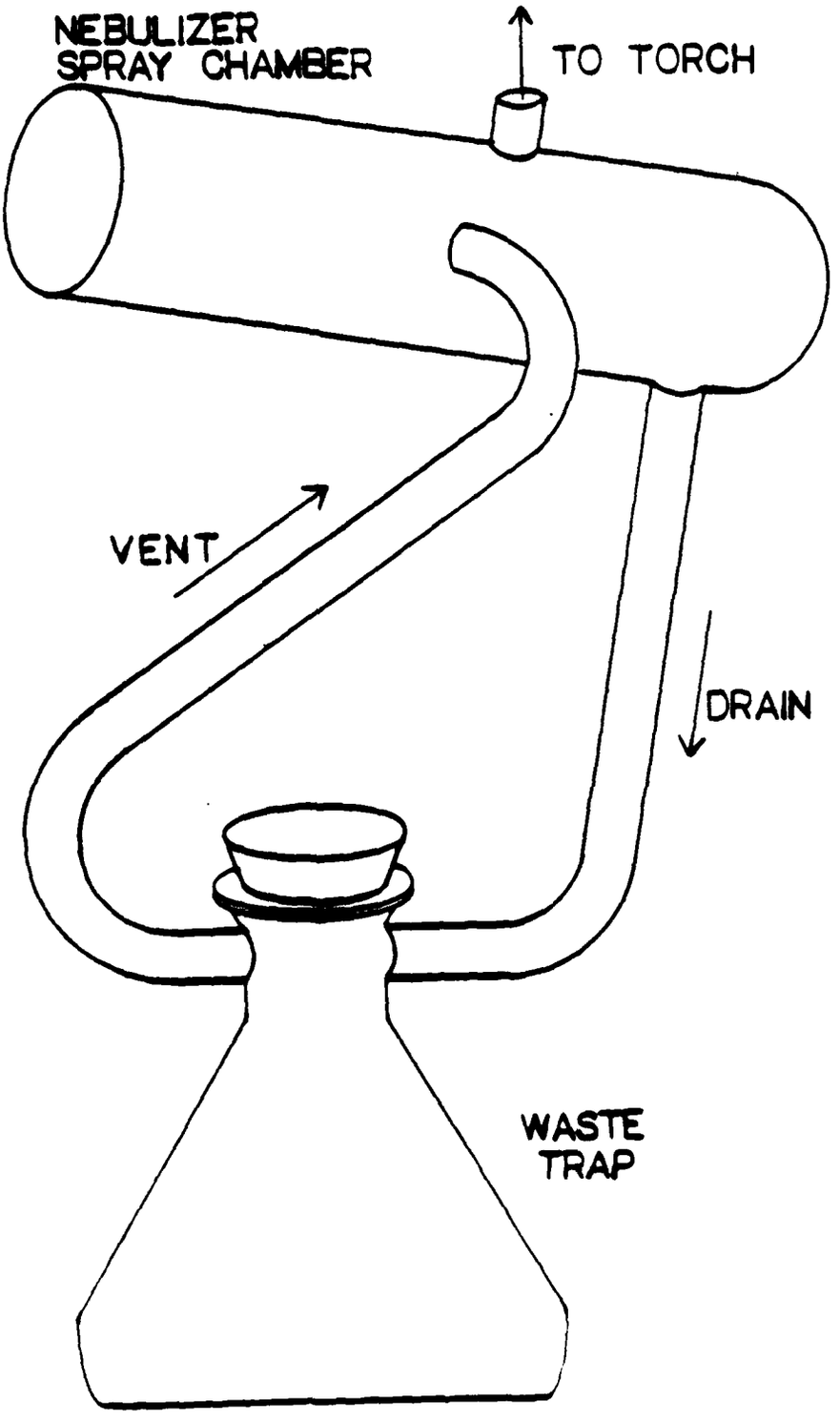

Figure 3

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